

STRUCTURE-PERFORMANCE RELATIONSHIPS IN ORGANOTIN MERCAPTIDE STABILIZERS

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Abstract- An attempt is made to illustrate the variables that need to be considered when undertaking a study of organotin mercaptide derivatives used for the stabilization of polyvinyl chloride. A mechanistic route involving coordination is offered as the most likely explanation of observed stabilizer performance. The type of alkyl group attached to tin as well as the number of such groups in the stabilizer molecule has a profound effect on the ability of the tin atom to coordinate labile chlorine atoms in the polymer. Of perhaps equal importance is the structure of the mercaptide portion of the stabilizer which affects not only the primary coordination chemistry, but secondary stabilization reactions such as free radical addition to unsaturated groups and antioxidation.

INTRODUCTION

The rapid growth of the rigid polyvinyl chloride industry in the United States in large part is due to the introduction and subsequent developments that have occurred in the area of organotin mercaptide heat stabilizers. These sulfur-containing organotin compounds utilized for the prevention of color formation during high temperature processing of the polymer, have evolved to the point where specific compositions are employed depending on such factors as the application, the manufacturing process and the economics of use. Indeed, the development of organotin mercaptide stabilizers for these specific applications and processes has served to promote further development in such areas as lubrication, compounding and machinery technology.

The context in which stabilizer candidates are evaluated has changed and it is not surprising, therefore, that products which were of little or no interest 15 years ago (when, for example, 2 parts of stabilizer were used per hundred parts of PVC resin in single-screw pipe extrusions) are of great interest today (in multi-screw pipe extrusions using less than 0.5 part of stabilizer).

Early investigations revealed that organotin and, in particular, dibutyltin derivatives of mercaptoacetic acid esters (or thioglycolic acid esters) imparted outstanding color retention and long-term heat stability to rigid PVC compounds both clear and pigmented (1-3). As competition among the stabilizer manufacturers increased, modifications began to appear in the standard product, dibutyltin bis(isooctyl mercaptoacetate), which resulted in improved retention of initial color. It soon became apparent that the use of monobutyltin tris(isooctyl mercaptoacetate) offered advantages in color stabilization while being deficient in long-term heat stability. When the low toxicity of di-n-octyltin bis(isooctyl mercaptoacetate) became recognized, it allowed the advantages of organotin mercaptide stabilizers to be extended to the manufacture of PVC articles intended for food contact applications (4). Butyltins and octyltins were later joined by methyltins and, most recently, by a class of compounds known as estertins (5,6). Attention had also turned to the nature of the mercaptan compound used to derivatize the alkyltin, and along with mercaptoacetates and straight-chain mercaptides came mercaptopropionates (7) and esters of mercaptoalcohols (8,9). Ways to increase the tin content of liquid stabilizers were discovered which resulted in so-called high efficiency tin mercaptides (10,11). Thus, by selective variation in the nature and degree of alkylation of tin, tin content, type of mercaptan, and numerous "tricks of the trade", a host of products are available today for such applications as extruded pipe, profiles and siding, calendered and extruded sheet, blow-molded containers and injection molded fittings.

It is the intent herein to illustrate the structural variations among the organotin mercaptide stabilizers and relate this to performance in model PVC formulations, commenting

where possible on their mechanism of action.

DISCUSSION

If one considers the series $R_4\text{Sn}$, $R_3\text{SnSR}'$, $R_2\text{Sn}(\text{SR}')_2$, $\text{RSn}(\text{SR}')_3$, $\text{Sn}(\text{SR}')_4$, it is apparent

from examination of the static heat stability test results in a rigid PVC system that the degree of alkylation of tin is directly related to the type of degradation observed. Using butyltin mercaptoacetates, the performance of dibutyltin bis(isooctyl mercaptoacetate), $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{C}_8\text{H}_{17})_2$, may be taken as standard. The two extreme case compounds,

tetrabutyltin and tin tetra(isooctyl mercaptoacetate), provide no stability, the former behaving as though no stabilizer was present and the latter giving severe early blackening characteristic of strong Lewis acids. These results may be rationalized in terms of a coordination mechanism involved in stabilization by organotin compounds. The reaction of organometallic compounds (including catalysis) in a polar medium, such as organotin compounds in molten PVC, involves coordination and that coordination of labile chlorine atoms in a PVC molecule by the tetravalent (hexacoordinate) organotin compound with subsequent displacement and/or rearrangement seems the primary mode of action (Fig.1)(12). Monobutyltin tris(isooctyl mercaptoacetate) combines improved early color with shortened long-term

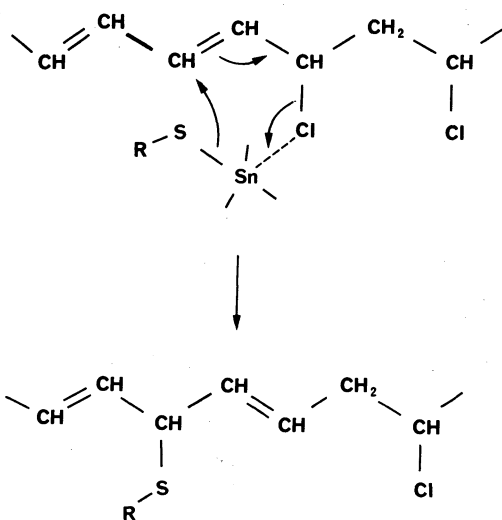


Fig. 1 Coordination of allylic chlorine by organotin mercaptide with subsequent rearrangement to a non-allylic structure.

stability. This is due to its intermediate Lewis acid character between that of dibutyltin bis(isooctyl mercaptoacetate) and tin tetra(isooctyl mercaptoacetate). The decreased effectiveness of tributyltin isooctyl mercaptoacetate may be ascribed to the added hindrance to coordination by the tin atom due to the presence of a third alkyl (butyl) group. Additionally, the role of trialkyltin derivatives in PVC stabilization have been nil due to toxicity considerations. The dynamic heat stability test results on the same series of compounds clearly shows the effect of Lewis acid character on the enhancement of degradation as evidenced by the development of cross-linking. (Fig. 2)

One familiar with the role of barium-cadmium and calcium-zinc in stabilizers of that type may prefer to draw an analogy with the organotins. Dialkyltin derivative performance may be likened to that of barium or calcium salts which provide good long-term stability. Barium and calcium chlorides are not Lewis acids while dialkyltin dichlorides are only weak Lewis acids. On the other hand, monoalkyltin derivative performance may be likened to that of cadmium or zinc salts which provide good early color but poor long-term stability. Cadmium, zinc and stannic chlorides are strong Lewis acids while monoalkyltin trichloride is of intermediate Lewis acid strength. The addition of certain Lewis acids and monoalkyltin chlorides are known to improve the color stability performance of dialkyltin mercaptide stabilizers (13,14). Like the cadmium and zinc containing stabilizers, monoalkyltin compounds will respond to the addition of organophosphite (for improved early color) and epoxidized oils (for increased long term heat stability) although not as dramatically.

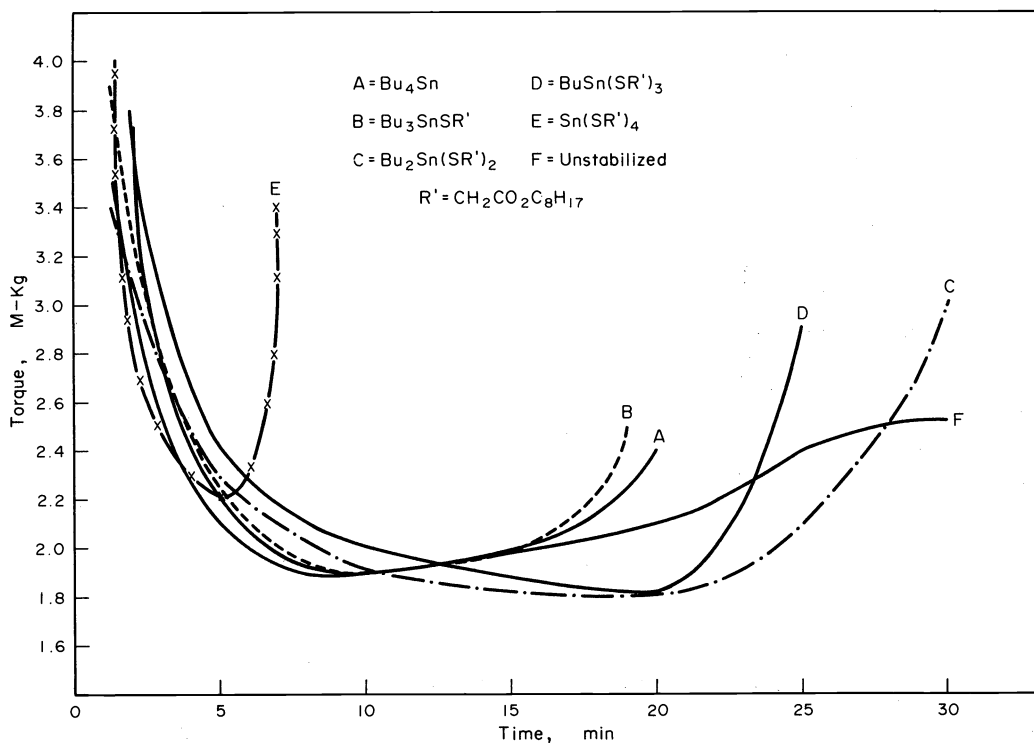


Fig. 2 Brabender stability-190°C, 50 rpm, 60g charge. Formulation-PVC, 100.0; ester wax, 0.5; stabilizer, 1.5.

Whether the alkyl group attached to tin is methyl, butyl, octyl, or carbomethoxyethyl would appear to have minor significance in that all four types may be satisfactorily employed in rigid PVC manufacture. In the United States it is the methyltin and butyltin types which predominate. Due to their higher cost, octyltin derivatives are utilized only where FDA approval is required, thus severely limiting their market. The estertins being recent introductions will be successful to the extent that they can compete with the established methyltin and butyltin stabilizers on a cost-performance basis and penetrate the market.

However, differences in performance do exist which are dependent on the alkyl substituent present and which must be taken into consideration by stabilizer manufacturers when developing new products and by end users when formulating and processing PVC compounds with these products. In the case of dialkyltin bis(isooctyl mercaptoacetate), as the alkyl chain length decreases from octyl to methyl, the stabilizers become increasingly compatible with the resin and, in fact, become better plasticizers for the resin since a greater part of the stabilizer molecule is the solvating ester isooctyl mercaptoacetate. This is manifested by lower melt viscosities and often lubrication adjustments are required when changing stabilizers. The estertins also demonstrate increased compatibility in PVC due to the presence of a polar ester group in the alkyl chain. Methyltin stabilizers appear to be more sensitive to the amount of monomethyltin present in the product. Put another way, less monomethyltin species is required for color improvement than is the case with butyltins or octyltins. This may be explained by the greater Lewis acid strength of monomethyltin trichloride (13) and by the enhanced ability of methyltin compounds to coordinate labile chlorine atoms in the PVC molecule due to less steric hinderance offered by the smaller methyl groups compared to the bulkier butyl and octyl groups. This steric effect is most pronounced when comparing methyltin derivatives with butyltin analogs as catalysts in the production of polyurethanes (15). Moreover, the thermal stability of dimethyltin bis(isooctyl mercaptoacetate) itself is superior to the dibutyltin, dioctyltin, and diestertin analogs as demonstrated in an elevated temperature stability test under anerobic conditions. Breakdown of the stabilizer occurs less readily in a press stability test indicating the suitability of this methyltin stabilizer for injection molding applications.

For many years, the principal mercaptan used in organotin stabilizer compositions was isooctyl mercaptoacetate. Specialty applications where a more highly lubricating stabilizer was desirable called for the use of dodecyl mercaptan. The linear aliphatic chain with no compatibilizing ester groups such as are present in isooctyl mercaptoacetate provided a greater degree of lubrication. However, the yellow color obtained with dibutyltin bis(dodecyl mercaptide) precluded its use for most applications. The ability of the tin atom in dibutyltin bis(dodecyl mercaptide) to coordinate labile chlorine atoms in PVC is evidently inferior to that in dibutyltin bis(isooctyl mercaptoacetate) with subsequent poorer performance. Dibutyltin bis(isooctyl mercaptoacetate) is an internally coordinated

compound (Fig. 3) the structure of which facilitates coordination of labile chlorine atoms,

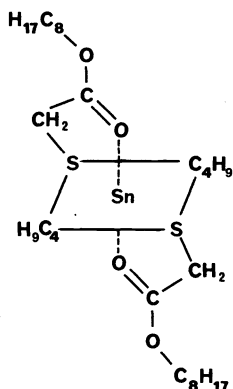


Fig. 3 Internally coordinated structure of dibutyltin bis(isooctyl mercaptoacetate).

while the lack of any restrained configuration in dibutyltin bis(dodecyl mercaptide) results in steric hinderance to coordination by the tin atom. If one compares dibutyltin bis(dodecyl mercaptide) with the dimethyltin analog, one observes significantly improved color stability with the dimethyltin compound presumably due, again, to substantially decreased steric hinderance about the tin atom. When dibutyltin compounds derived from esters mercaptoethanol were evaluated, color stability results were obtained similar to that of isooctyl mercaptoacetate.

As was mentioned earlier, most rigid PVC compounds were processed on single-screw extruders and typical stabilizer levels were in the range of 2.0-3.0 parts per hundred parts of PVC resin (phr). With the advent of twin and multi-screw extrusion techniques principally for the production of PVC pipe, characterized by highly externally lubricating formulations and run at lower processing temperatures, stabilizer levels fell dramatically to well below 1.0 phr. Due to continued advances in extruder design, typical stabilizer levels in today's single and multi-screw formulations are approximately 0.8 phr for the former and 0.4 phr for the latter cases. Long-term, high temperature heat stability was no longer of prime concern and attention turned to the maintenance of good initial color. Now began the era of the monoalkyltin mercaptides.

Stabilizers high in monoalkyltin content were introduced consisting essentially of methyltin and butyltin isooctyl mercaptoacetates. When a high monomethyltin content stabilizer derived from a mercaptoethanol ester was demonstrated to provide outstanding early color and color retention in white pipe (9), the industry quickly accepted this departure from the traditional mercaptoacetate products. Keep in mind that these rigid PVC formulations contain significant amounts of calcium stearate as part of the lubrication system relative to the tin stabilizer, and this further serves to balance any tendency of monoalkyltins to cause early blackening. Although the mercaptoethanol esters have a polar, compatibilizing functional group, they are for the most part based on fatty acid esters and, therefore, are more lubricating than the mercaptoacetate products.

A parallel development in organotin stabilizer technology was the discovery that organotin sulfides could partially replace the mercaptides in certain stabilizer compositions, thereby allowing the preparation of high tin content products. Neither the sulfides of dialkyltin nor monoalkyltin by themselves are particularly good stabilizers in spite of their very high tin content. The polymeric nature of these compounds perhaps acts as a hinderance to their coordinating ability. The type of performance obtained with the alkyltin sulfides, nevertheless, is qualitatively analogous to the mercaptides. That is, dialkyltin sulfide imparts long-term stability whereas monoalkyltin sulfide (alkylthio-stanoic acid anhydride) is poor in this respect. However, when the alkyltin sulfides are used in conjunction or admixture with the alkyltin mercaptides, a synergistic effect in performance is obtained. Thus, the combination of dialkyltin bis(isooctyl mercaptoacetate) with monoalkyltin sulfide (11), or monoalkyltin tris(isooctyl mercaptoacetate) with dialkyltin sulfide (16), affords high tin content products with powerful stabilizing properties.

Another approach to such a stabilizer composition would be a direct synthesis from a proper combination of monobutyltin trichloride and dibutyltin dichloride which is reacted with a suitable quantity of isooctyl mercaptoacetate and sodium sulfide (Fig. 4)(17). Suffice it to

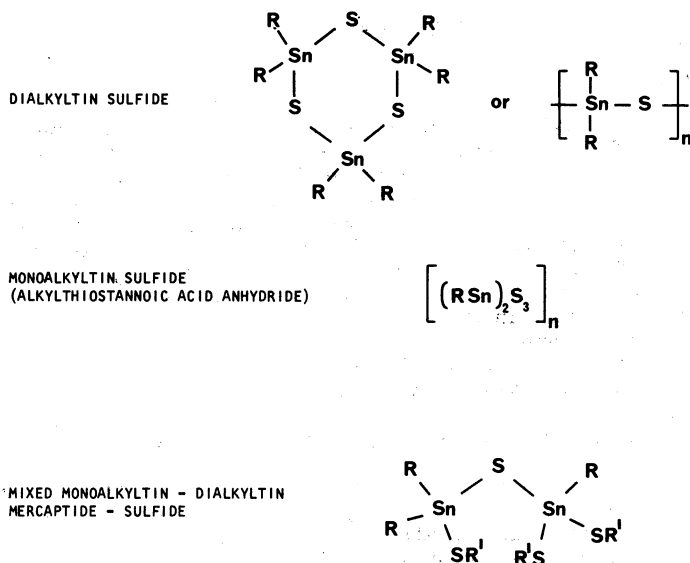


Fig. 4 Organotin sulfides.

say that this technology in practice has been extended to include methyltins as well as butyltins and mercaptoethanol esters as well as isooctyl mercaptoacetate.

Organotin mercaptides react rapidly with strong mineral acids to form organotin mineral acid salts and free mercaptan. To the extent that a tin stabilizer reacts with hydrochloric acid evolved from PVC, Mercaptans will be produced and if the stabilizer contains sulfide sulfur the potential for the formation of hydrogen sulfide exists. Free mercaptan compounds, whether formed by reaction of the stabilizer with hydrochloric acid, or initially present in the commercial stabilizer, may react with unsaturation present or developing in the PVC molecule. Addition of a sulphydryl group to a conjugated double bond system will destroy that conjugated system thus reducing or eliminating a chromophoric group from the polymer (Fig. 5). Esters of mercaptoacetic acid react considerably more rapidly with

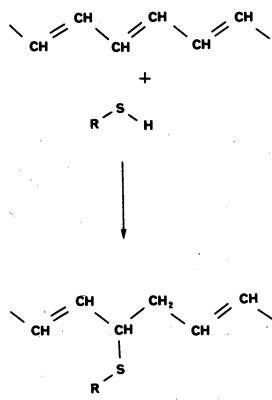
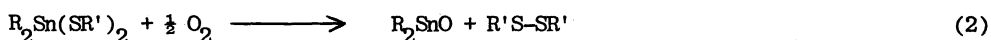
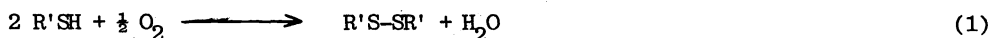


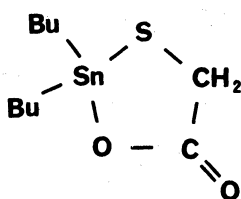
Fig. 5 Mercaptan addition to conjugated double bond system with destruction of conjugation.

double bond systems, presumably via a free radical mechanism, than do aliphatic mercaptans (18). This provides an additional explanation for the observed superiority of dibutyltin bis(isooctyl mercaptoacetate) over dibutyltin bis(dodecyl mercaptide). To the degree that oxidation plays a role in the degradation of PVC, mercaptans and organotin mercaptides themselves act as antioxidants, being oxidized to disulfides (equations 1 and 2).

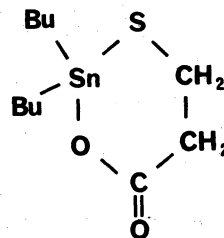


In discussing the role of isooctyl mercaptoacetate in PVC stabilization, one might consider the function of unesterified mercaptoacetic acid. Mercaptoacetic acid, if added to dibutyltin bis(isooctyl mercaptoacetate), will cause the development of a crystalline precipitate. The composition of this precipitate is known to be the dibutyltin salt of mercaptoacetic acid formed by displacement of isooctyl mercaptoacetate from its dibutyltin salt. It is this same crystalline material that is occasionally observed in samples of commercial stabilizers and is believed to occur when excessive hydrolysis of isooctyl mercaptoacetate takes place during the manufacture of stabilizer and the solubility of the dialkyltin mercaptoacetic acid salt in the stabilizer is exceeded. Investigation of the performance of this salt in PVC reveals the fact that although its tin content is quite high, its stabilizing effectiveness is low. A comparison of dibutyltin mercaptoacetate with dibutyltin 3-mercaptopropionate quickly shows the strong stabilizing properties of the latter compound. This seems surprising in that a comparison of the dibutyltin salts of isooctyl mercaptoacetate and isooctyl-3-mercaptopropionate shows no significant differences.

Empirical observations of the two salts reveals that the mercaptoacetate is higher melting and more difficult to solubilize than the mercaptopropionate and does not titrate as readily with potassium iodate, indicating a less available sulfur. Although conclusions based on spectral data point to a linear polymeric structure (19), one might argue that a 5-membered ring structure for the mercaptoacetate salt is more stable than a corresponding 6-membered ring for the mercaptopropionate (Fig. 6) and, hence, the lesser tendency of the former to enter into stabilizing reactions.



DIBUTYL TIN
MERCAPTOACETATE
M.P. 193°-195°C



DIBUTYL TIN
3-MERCAPTOPROPIONATE
M.P. 118°-120°C

Fig. 6 Dibutyltin salts of mercaptoacids.

REFERENCES

1. W.E. Leistner and A.C. Hecker, U.S. Patent 2,641,596 (June 9, 1953).
2. W.E. Leistner and O.H. Knoepke, U.S. Patent 2,641,588 (June 9, 1953).
3. E.L. Weinberg and E.W. Johnson, U.S. Patent 2,648,650 (Aug. 11, 1953).
4. Federal Register of The Congress of the United States 33, 14, Title 21, Part 121, Subpart F (Jan. 20, 1968).
5. R.E. Hutton and V. Oakes, Advances In Chemistry Series, 157, p. 123-133 (1976).
6. D. Lanigan and E.L. Weinberg, ibid., p. 134-154.
7. G.P. Mack and E. Parker, U.S. Patent 3,027,350 (Mar. 27, 1962).
8. W.E. Leistner and A.C. Hecker, U.S. Patent 2,870,119 (Jan. 20, 1959).
9. T.G. Kugele, U.S. Patent 4,062,881 (Dec. 13, 1977).
10. O.S. Kauder and M.W. Pollock, U.S. Patent 3,565,930 (Feb. 23, 1971).
11. J.B. Gottlieb and W.E. Mayo, U.S. Patent 3,424,717 (Jan. 28, 1969).
12. A.H. Frye, R.W. Horst, and M.A. Paliobagis, J. Polymer Sci., A-2, p. 1812 (1964).
13. H.O. Wirth, H.A. Muller, and W. Wehner, J. Vinyl Tech., I, No. 1, p. 53-54 (1979).
14. W.A. Larkin, U.S. Patent 3,715,333 (Feb. 6, 1973).
15. L.R. Brecker, Plast. Eng., 33, No. 3, p. 39 (1977).
16. W.A. Larkin and R.C. Ringwood, Jr., U.S. Patent 4,183,846 (Jan. 15, 1980).
17. L.R. Brecker, U.S. Patent 3,565,931 (Feb. 23, 1971).
18. R.C. Poller, Advances In Chemistry Series, 157, p. 179 (1976).
19. C.H. Stapfer and R.H. Herber, J. Organometal. Chem., 56, p. 175-183 (1973).